# Extraction of uranium(VI) with N-octanoylpyrrolidine in sulfonated kerosene

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**Abstract** Extraction of uranium with N-octanoylpyrrolidine (OPOD) in sulfonated kerosene from aqueous nitric acid media has been studied. The dependence of the extraction distribution ratios on the concentrations of aqueous nitric acid, extractant, salting-out agent and the temperature was investigated. The constitution of extracted complex was established, and the related thermodynamic functions were calculated.

**Keywords** N-octanoylpyrrolidine, Solvent extraction, Uranium(VI)

**CLC numbers** O615, O615.11

## 1 INTRODUCTION

Amide extractants have resistance to hydrolysis, radiolysis and their degradation products do not interfere severely in the separation process. They can burn completely, without any solid waste. Furthermore, they extract actinides from nitric acid media effectively. Therefore, amide extractants have been proposed as an alternative to TBP for the reprocessing of nuclear fuel.[1] However, when the acidity or concentration of uranium is high, the system presents third phase easily. In order to prevent it from forming third phase, we must increase the length of carbon chains of substituent on which carbonyl and nitrogenous atom are connected.[2~5] However, it will make molecular weight of extractant increase and the extractants are hard to dissolve in aliphatic solvent. Therefore, cyclic amides such as N-octanoylpyrrolidine (OPOD) have been synthesized instead of straight-chain amide to decrease molecular weight and improve extraction performance in our latoratory. This new type of extractant has not been reported in the literatures. In this paper, the influence of some factors on uranium extraction with the OPOD is studied in detail.

## 2 EXPERIMENTAL

### 2.1 Synthesis of N-octanoylpyrrolidine

The OPOD was synthesized in our laboratory as it was not available from market. The synthesis path is expressed as follows:

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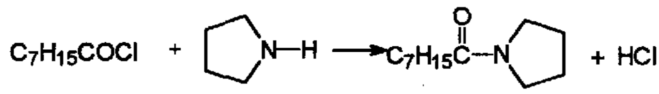
$$C_7H_{15}COOH + SOCl_2 = C_7H_{15}COCl + SO_2 + HCl$$




The purity of product was checked by IR spectrometry, $^1$HNMR spectrometry and elemental analysis. The product can be applied directly in the experiments.

### 2.2 Instruments and reagents

Type 752 UV grating spectrometer (Shanghai Third Analysis Instrument Factory), Vibrator (made by Yancheng Science Instrument Factory, Jiangsu Province) with vibration frequencies is about 4.5 Hz, temperature control is achieved in a cage and precision is about ±1K. The dilution is sulfonated kerosene. The other reagents are of analytic purity.

### 2.3 Experimental methods

Extraction was carried out by shaking equal volumes of the OPOD diluted with sulfonated kerosene and uranyl nitrate solution containing nitric acid in a stopper tube at 293±1 K for 2 h. Phase disengagement was rapidly obtained by centrifugation. Uranium(VI) ion in aqueous solution was analyzed by the Arsenazo-III spectrophotometric method and uranium(VI) concentration in organic solution was calculated from the difference between total quantity and its quantity in aqueous solution.

## 3 RESULTS AND DISCUSSION

### 3.1 Effect of $HNO_3$ concentration

Fig.1 shows that as concentration of nitric acid increases, the distribution ratio of uranium(VI) is increased. After reaching the maximum, then decreased. The reason is that, under the condition of higher concentration of nitric acid, some complex anions such as $[UO_2(NO_3)_3]^-$ can be formed, which make uranium extraction more difficult. Furthermore, because more complexes between $HNO_3$ and extractant are formed at higher $HNO_3$ concentration, concentration of extractant is decreased. It also makes distribution ratios decrease.

### 3.2 Effect of extractant concentration

The extraction of uranium(VI) from 1.5 mol/L nitric acid aqueous medium by the OPOD in sulfonated kerosene increases with the increase of extractant concentration.

The extraction reaction in this system can be expressed as follows:

$$UO_2^{2+} + 2NO_3^- + nOPOD_{(o)} = UO(NO_3^-)_2(OPOD)_{n(o)}$$

$$\text{Equilbrium constant } K_{ex} = \frac{[UO_2(NO_3^-)_2(OPOD)_n]_{(o)}}{[UO_2^{2+}][NO_3^-]^2[OPOD]_{(o)}^n}$$

$$\lg D = \lg K_{ex} + 2\lg[NO_3^-] + n\lg[OPOD]_{(o)}$$

The results are shown in Fig2. The plots of lgDu vs $\lg[OPOD]_{(o)}$ gives a slope of 2.2, close to 2, which indicates $n$=2. Therefore, the extracted complex may be $UO_2(NO_3)_2(OPOD)_2$, $K_{ex}$ is measured to be 2.506 $mol^{-4}\cdot dm$.[6]

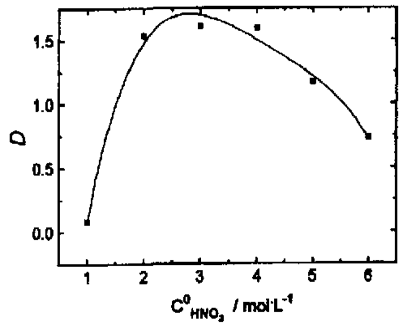



**Fig.1** Du vs [$HNO_3$]
$C^o_{OPOD}$=0.3 mol/L, $T$=293±1 K
$C^o_{[UO_2]^{2+}}$=4.00×$10^{-3}$ mol/L

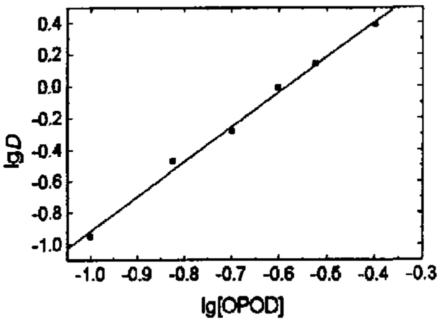



**Fig.2** Du vs [OPOD]
$C^0_{HNO_3}$=1.5 mol/L, $T$=293±1 K
$C^0_{[UO_2]^{2+}}$=4.00×$10^{-3}$ mol/L

### 3.3 Effect of salting-out agent concentration

Table 1 shows the influence of the concentration of lithium nitrate on the distribution ratio of U(VI). The extraction of uranium(VI) increases rapidly with increasing $LiNO_3$ concentration. $LiNO_3$ here plays an important role not only as a salting-out agent which increases the uranium(VI) activity by hydration of $Li^+$ but also as a homoion, shifting the extraction equilibrium to the right.

**Table 1** Variation of U distribution with concentration of $LiNO_3$ in aqueous solution

| Nitrate lithium/mol·L$^{-1}$ | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $D$ | 0.03 | 1.70 | 4.72 | 21.5 | 60.8 |

$C^0_{OPOD}$=0.3mol/L, $C^0_{HNO_3}$=3 mol/L, $C^0_{[UO_2]^{2+}}$=4.00×$10^{-3}$ mol/L, T=293±1 K

### 3.4 Effect of temperature

Extraction of Uranium(VI) from 3 mol/L $HNO_3$ aqueous medium with 0.3 mol/L OPOD was investigated at different temperatures. The data are shown in Fig3. It can be seen that $\lg D$ increased linearly with $1/T$. This indicates that the extraction reaction is an exothermic reaction and low temperature is beneficial to the extraction reaction. According to Vant Hoff equations:

$$\frac{\partial \lg D}{\partial(1/T)} = -\frac{\Delta H^0}{2.303R}$$

$$\Delta G^0 = -RT\ln K_{ex}$$

$$\Delta G^0 = H^0 - T \cdot \Delta S^0$$

By Fig.3 , the value is calculated to be

$$\Delta H^0 = -35.09\,\mathrm{KJ/mol}$$

$$\Delta G^0 = -2.688\,\mathrm{KJ/mol}$$

$$\Delta S^0 = -110.6\,\mathrm{J/(mol \cdot K)}$$

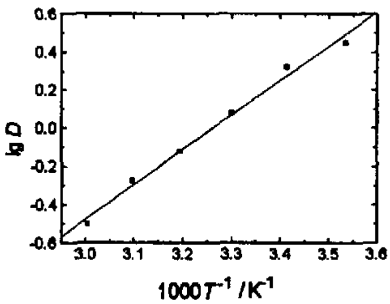



**Fig.3** $D$ vs $T^{-1}$
$C^0_{OPOD}$=0.3mol/L, $C^0_{HNO_3}$=3 mol/L,
$C^0_{(UO_2)^{2+}}$=$4.00\times10^{-3}$ mol/L

## 4 CONCLUSIONS

OPOD in sulfonated kerosene can extract U(VI) from nitric acid media and the extracted complex can be expressed as $UO_2(NO_3)_2(OPOD)_2$. The value of $\Delta H$ is negative which means that decreasing the temperature will increase the distribution under the conditions studied. During the experiments there is no third phase formation and the mixed phases are separated quickly, which also indicated that the OPOD is a promising extractant for practical application of nuclear industry.

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